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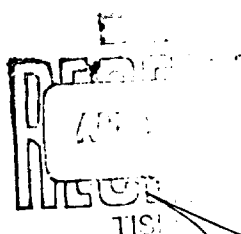
1 October - 31 December 1963

ELECTROCHEMICAL STUDIES IN THE
SYNTHESIS OF N-F COMPOUNDS

Contract No. Nonr-4054(00)
Research Project No. RR001-06-02
ARPA Order No. 399, Program Code No. 2910

March 31, 1964

TRACOR

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TRACOR, Inc.

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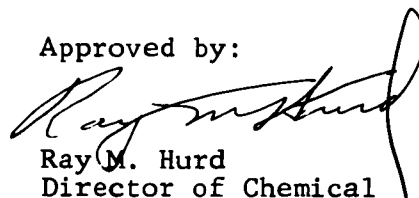
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Abstract

This report describes work which has been devoted to the development of suitable reference and working electrodes for use in electrochemical fluorination studies in anhydrous HF.

Of several metal-metal fluoride combinations studied, including nickel, platinum, aluminum, and mercury, as possible reference electrodes, the Hg/Hg_2F_2 is far superior with regard to reproducibility, stability, and reversibility and will be used in all future studies.

Investigations of possible working electrodes have involved aluminum, platinum, thallium, magnesium, and iron. Thallium corroded very rapidly in anhydrous HF; attempts were made to passivate thallium by anodic oxidation to Tl^{3+}, which forms a much less soluble fluoride than the Tl^+, but without success. Iron and platinum corrode less rapidly than thallium but yield very erratic anodic polarization curves with a high corrosion current. Aluminum and magnesium corrode very slightly, if any, after an initial period of dissolution which lasts about five hours in anhydrous HF. The aluminum acquires a highly resistive protective film, presumably AlF_3. Cathodic treatment destroys this film and initiates a rapid attack of the aluminum.

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ELECTROCHEMICAL STUDIES IN THE SYNTHESIS OF N-F COMPOUNDS

I.   INTRODUCTION

During the past quarter work has continued on the development of a reference electrode and corrosion resistant working electrode for use in the study of the electrochemical fluorination of NH_3 and N_2H_4 in anhydrous HF. The use of a reliable reference electrode is, of course, necessary to correlate anodic potentials with the kinetics of the electrochemical reaction. It is desirable to employ a working anode which exhibits a very low corrosion current on anodic polarization to avoid contamination of the HF solution, to preserve the electrochemical characteristics of the electrode, and to simplify interpretation of the electrochemical data.

The approach taken toward developing a reference electrode has consisted mostly of investigating various metal-metal fluoride systems with regard to the reproducibility of their open-circuit potentials, stability of the open-circuit potential with time, and reversibility on polarization. From results obtained during the past quarter, it is concluded that the Hg/Hg_2F_2 electrode in a suitable geometric configuration is by far the best system studied to date and meets all requirements as a reference electrode for future work planned.

The development of a suitable <u>working</u> electrode is still unresolved, although aluminum and magnesium show sufficient passivity to extend the experiments to fluorinating conditions. These metals are not entirely satisfactory because of the high resistivity of a protective coating composed of their fluorides; therefore, additional metals will be investigated at the same time fluorination studies are being made on aluminum and magnesium.

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II.   EXPERIMENTAL APPARATUS

Several improvements have been made in the equipment for handling anhydrous HF during this quarter. These improvements have resulted in greater purity of HF in the electrolytic cell, better reliability of the apparatus, and less elapsed time between experiments.

The purification procedure for HF consists of absorbing tank HF in a NaF trap maintained at $110^{\circ}C$. The resulting $NaHF_2$ is then decomposed at $200^{\circ}C$ and HF condensed in the electrolysis cell after discarding a portion of the trapped HF. In the past, the externally heated NaF trap was subject to frequent flow stoppages at the HF inlet presumably because of unequal distribution of heat and HF flow. These difficulties were corrected by surrounding the HF inlet port with a nickel screen which allowed the HF to contact a greater area of NaF pellets and by providing a heater well for a 1000 watt heater cartridge to allow heating the NaF trap internally and externally at the same time. Improvement in temperature control was also obtained by inserting a stainless steel sheathed thermocouple directly in the NaF pellets. The present configuration of the trap is shown in Figure 1.

The HF storage vessel shown in Figure 2 is equipped with a nickel anode for further purification of the HF by pre-electrolysis. The vessel serves as the cathode during electrolysis. In recent experiments, pre-electrolysis has not been used because of indications that it increases the conductivity of the HF by corrosion of the nickel anode. The pre-electrolysis cell will be used again in the future if experiments show that the NaF trap fails to purify the HF sufficiently.

The apparatus was altered also to accommodate two experimental cells to speed the performance of experiments. Each cell can be operated independently of the other. The condensers on the electrolytic cells have been offset to allow the introduction
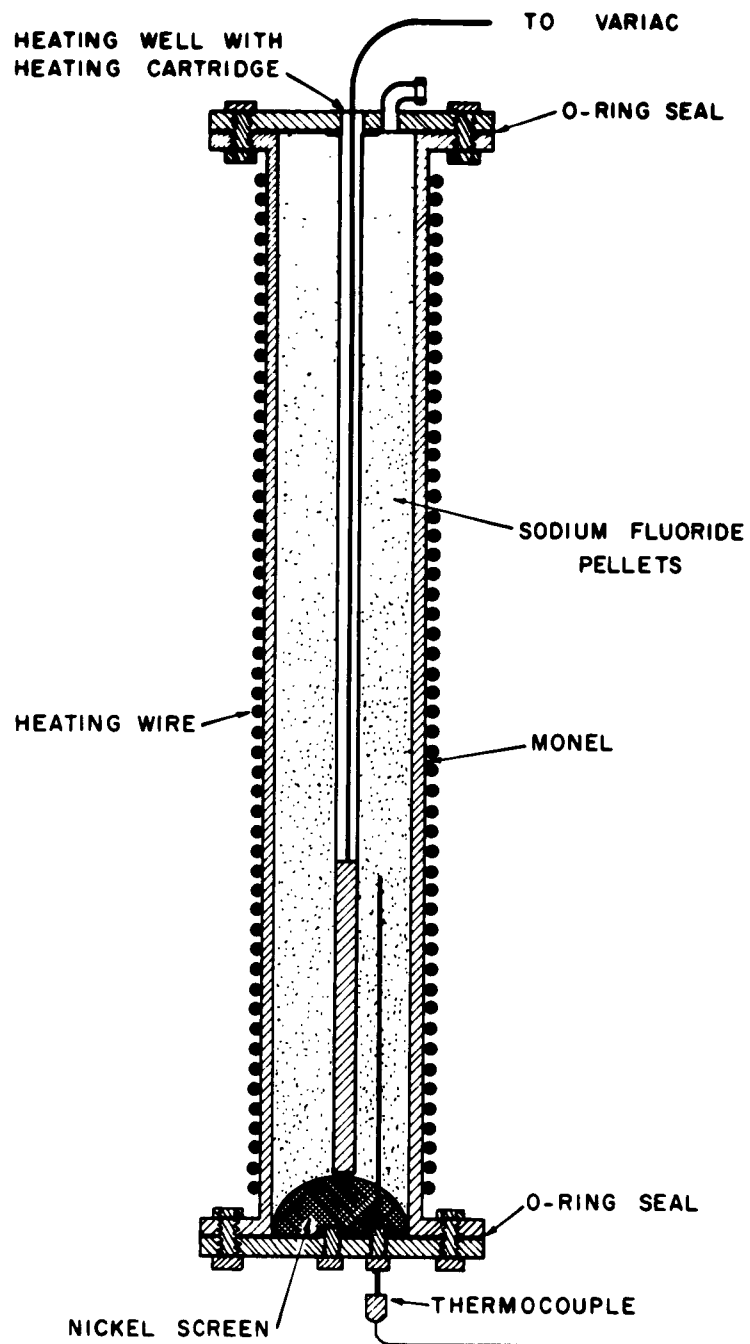
HEATING WELL WITH
HEATING CARTRIDGE

TO VARIAC

O-RING SEAL

SODIUM FLUORIDE
PELLETS

HEATING WIRE

MONEL

O-RING SEAL

THERMOCOUPLE

NICKEL SCREEN

Fig. I - HF TRAP

O-RING SEAL

TEFLON GASKET
SEAL

COLD FINGER

MONEL

TEFLON RING

NICKEL ELECTRODE

DISPOSAL

THERMISTOR
CASE

TEFLON
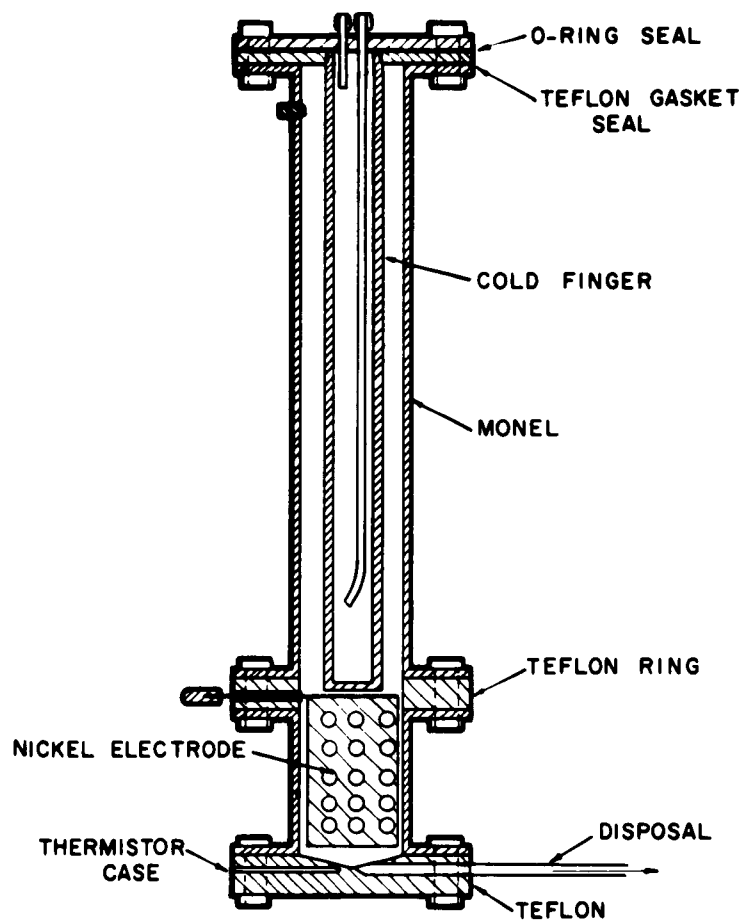
Fig. 2 - HF STORAGE VESSEL

of electrodes and/or solutes into the cell while it contains HF.
In this manner, electrodes can be changed without having to dump
the HF and refill the cell as was done previously. The conical
cover on the previous cell was replaced by a Teflon ring and
cap as shown in Figure 3. The ring was drilled and tapped at
six evenly spaced locations around its circumference to accommo-
date six Swagelok fittings for the following connections:

1. N_2 line
2. HF line (from NaF trap to cell)
3. Condenser line
4. Thermistor case
5. Nickel screen auxiliary electrode
6. Sight tube

The Teflon cap seals the cell and is fitted with connections
for three electrodes as shown in Figure 3. Thus, two working
electrodes and a reference electrode can be used simultaneously.
Figure 3 shows the cell accommodating a single working electrode
and two reference electrodes for experiments in which the stability
of one reference electrode under load was monitored with respect
to a reference electrode at open circuit. An assembled cell with
two reference electrodes and a working electrode is shown in
Figure 4. The same cell as installed with its cooling coil is
shown in Figure 5.

Two reference electrodes have been built to investigate
the behavior of various half-cell systems in anhydrous HF.
Construction details of the electrodes are shown in Figure 6
as used for the investigation of the Hg/Hg_2F_2 electrode. The
Hg/Hg_2F_2 electrode provides a stable reproducible potential in
anhydrous HF as shown by data presented later in this report.
It is necessary to build new electrodes each time the electrolysis
cell is disassembled because Hg_2F_2 is decomposed by moist air,
and because boiling HF in the Hg_2F_2 displaces part of the active
material out of the reference electrode holder. Addition of the

TEFLON CAP

REFERENCE ELECTRODE

WORKING ELECTRODE

N₂ SUPPLY

TEFLON RING

TO CONDENSER

TEFLON THERMISTOR
CASE

TEFLON N₂
LINE

NICKEL SCREEN

SIGHT
GLASS

TEFLON VESSEL
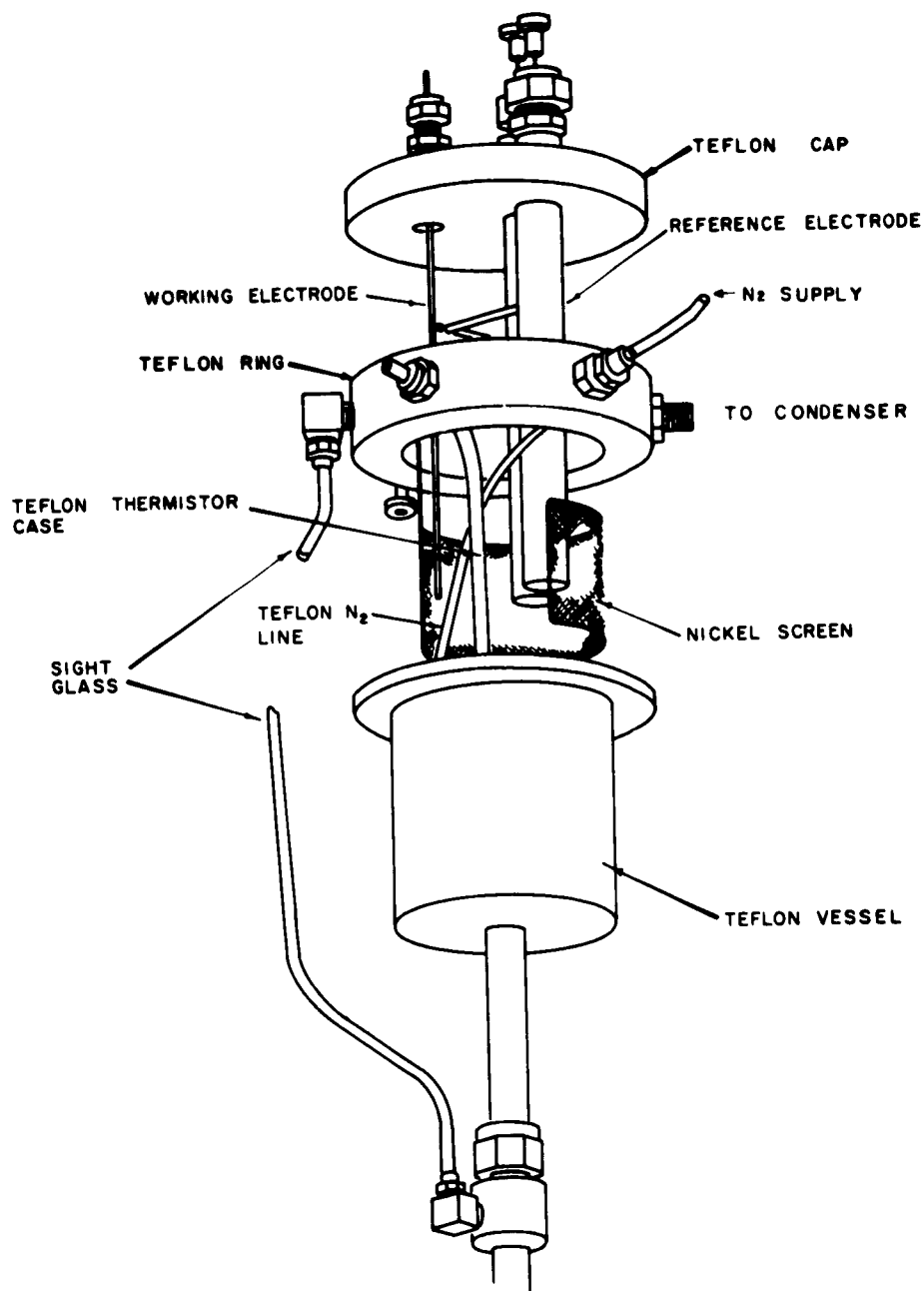
Fig. 3 -ELECTROLYTIC CELL
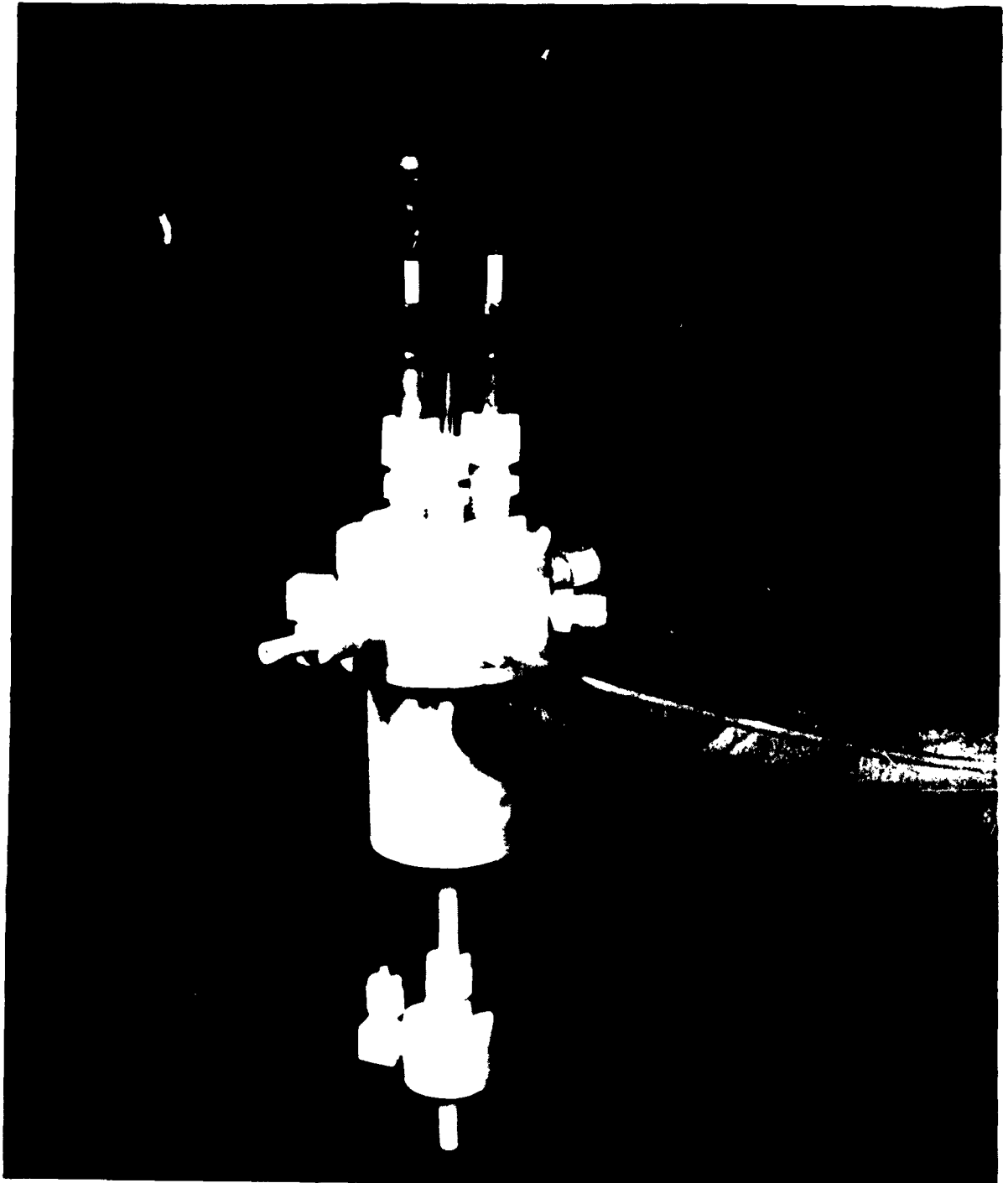
Fig. 4 - CELL ASSEMBLY

Fig. 5 – CELL INSTALLATION

BANANA CLIP

NICKEL WIRE

TEFLON ROD

REDUCER (KEL-F)

SWAGELOK MALE CONNECTOR

1/8" I.D. HOLE

TEFLON ROD DRILLED WITHIN 1/4" OF BOTTOM

1/16" I.D. TEFLON TUBING

POROUS TEFLON SEAL

MERCUROUS FLUORIDE

MERCURY
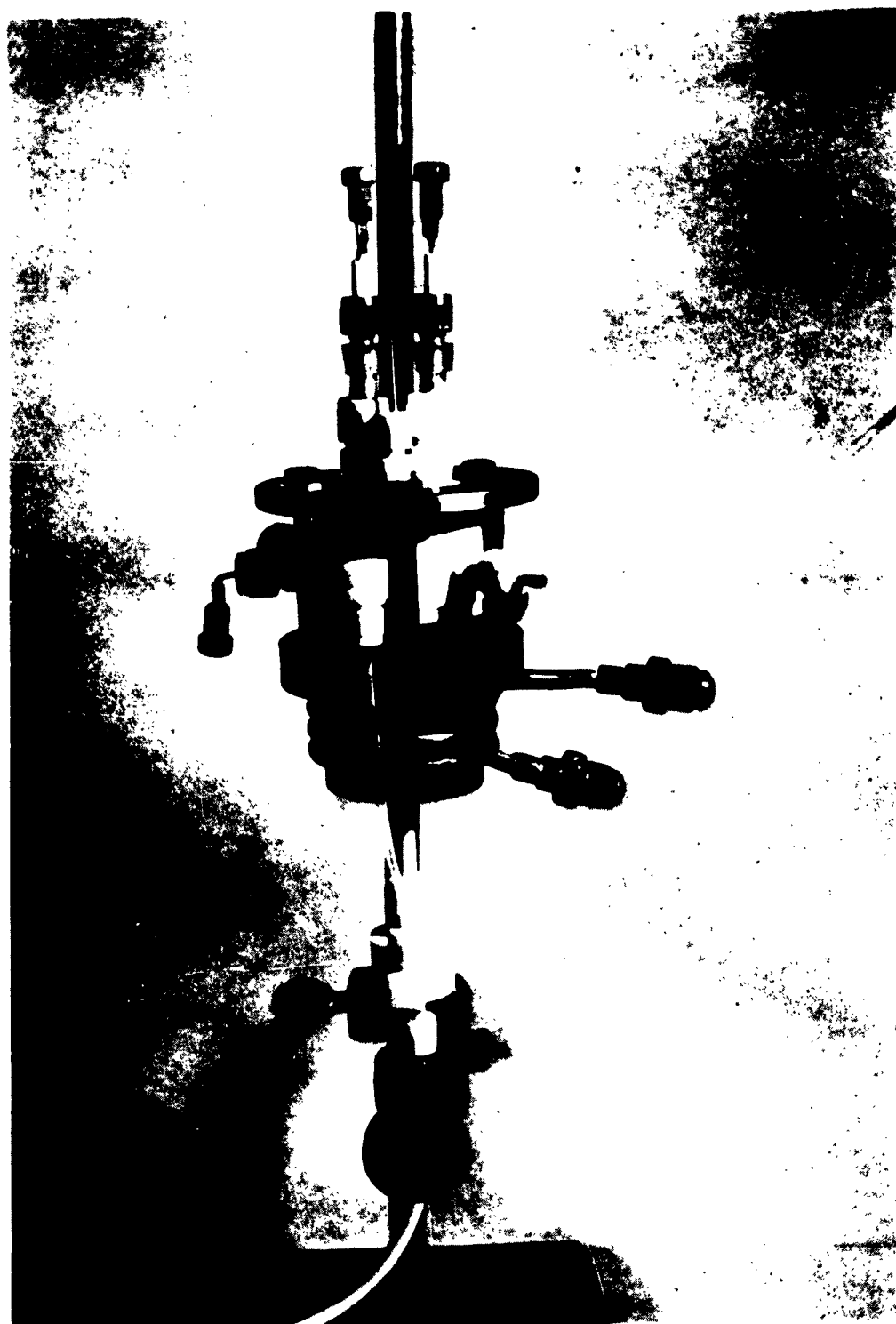
Fig. 6 - REFERENCE ELECTRODE Hg/Hg_2F_2

porous Teflon plug in the electrode helped retain the Hg_2F_2 but did not entirely solve the problem. It was noted that the cell should be open to the atmosphere when dumping in order to prevent HF from bubbling in the reference electrode holder. If under vacuum, the HF bubbling could displace some of the Hg_2F_2 or mercury.

Displacement of the Hg and Hg_2F_2 by boiling HF on filling the cell is avoided by allowing the electrode to reach temperature equilibrium with liquid HF before filling the cell. The reference electrode is assembled without HF and is then sealed into the electrolysis cell by the Swagelok male connector. Sufficient liquid HF is then introduced into the cell to immerse only the lower part of the electrode so none can enter the capillary side arm. About 30 minutes is then allowed for the electrode and liquid HF to reach temperature equilibrium ($-26^{\circ}C$) after which filling of t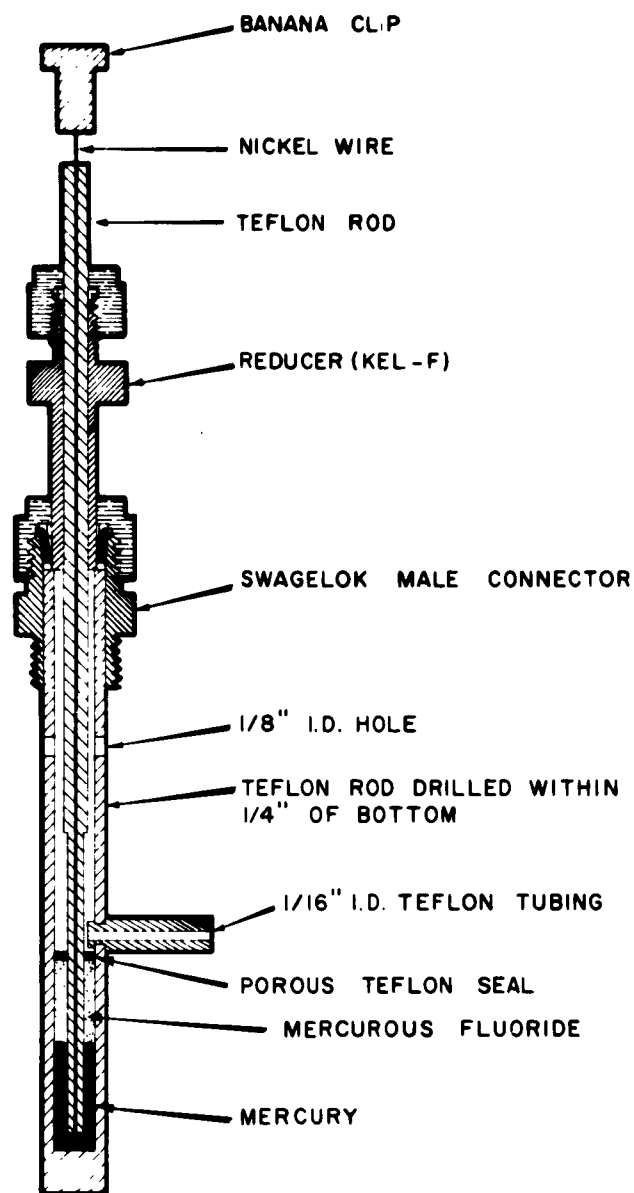he cell with HF is completed. Complete filling of the reference electrode is assured by provision of a 1/8" vent hole in the electrode holder above the HF liquid level.

The HF disposal system has been simplified during the last quarter for greater reliability. In the previous system, NaOH solution was circulated through an aspirator from a reservior by a small pump constructed of monel. The HF was mixed with the circulating NaOH solution through the vacuum side of the aspirator. The method worked very well when new; however, it later became subject to frequent stoppages because of plugging of the aspirator intake and leakage by the pump packing. These difficulties were overcome by the dump system now in use as shown in Figure 7. The aspirator is now powered by a water tap, eliminating the pump, and HF is passed into an evacuated flask where it is absorbed by a 25% NaOH solution. When all HF is removed from the system, pressures are equalized by a pressure relief value to prevent the NaOH solution from backing up into the experimental apparatus.

Fig. 7 - HF DISPOSAL SYSTEM

TO ASPIRATOR

PYREX VACUUM FLASK

VACUUM GAGE

NaOH

25%

PYREX VACUUM FLASK

PRESSURE RELEASE VALVE

POLYPROPYLENE VACUUM FLASK

POT

CELL I

CELL II

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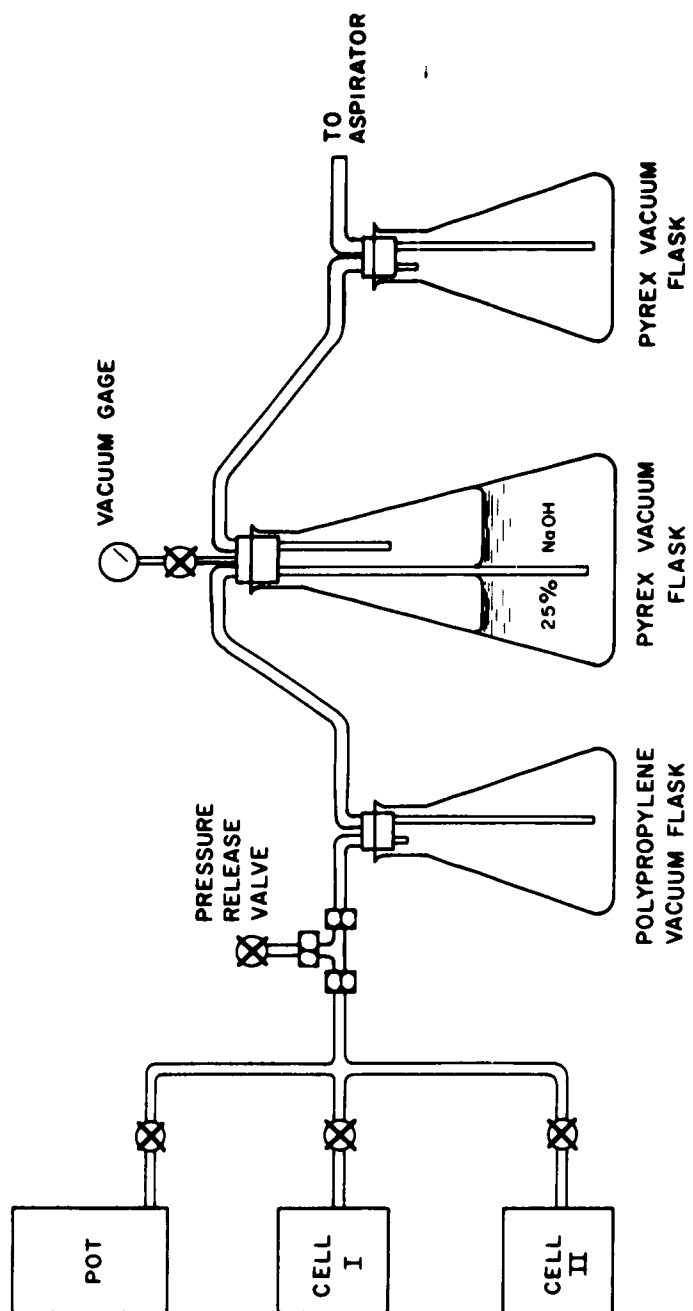
TRACOR, INC   170 Guadalupe St   Austin 1, Texas

The complete HF handling system as it is now being used is shown in Figure 8. The HF is first collected in a storage cylinder which is equipped with a sight tube for measurement of the volume of HF. It is then distilled into the NaF trap which is maintained at $110^{\circ}C$ as already described. After rejection of part of the HF from the trap to the disposal system, a portion is condensed in the electrolytic cells where the experiments are carried out.

Fig. 8 - HF HANDLING SYSTEM

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TRACOR, INC   DWG A729-67
AUSTIN, TEXAS 3/20/64 WEH/AA

III. REFERENCE ELECTRODES

The Hg/Hg_2F_2 reference electrodes used in this work are based on results given by Koerber and DeVries (1). The design of the Teflon electrode holder has been described already (see Figure 6). The electrodes have been sufficiently reproducible and stable and will be used in future electrochemical experiments.
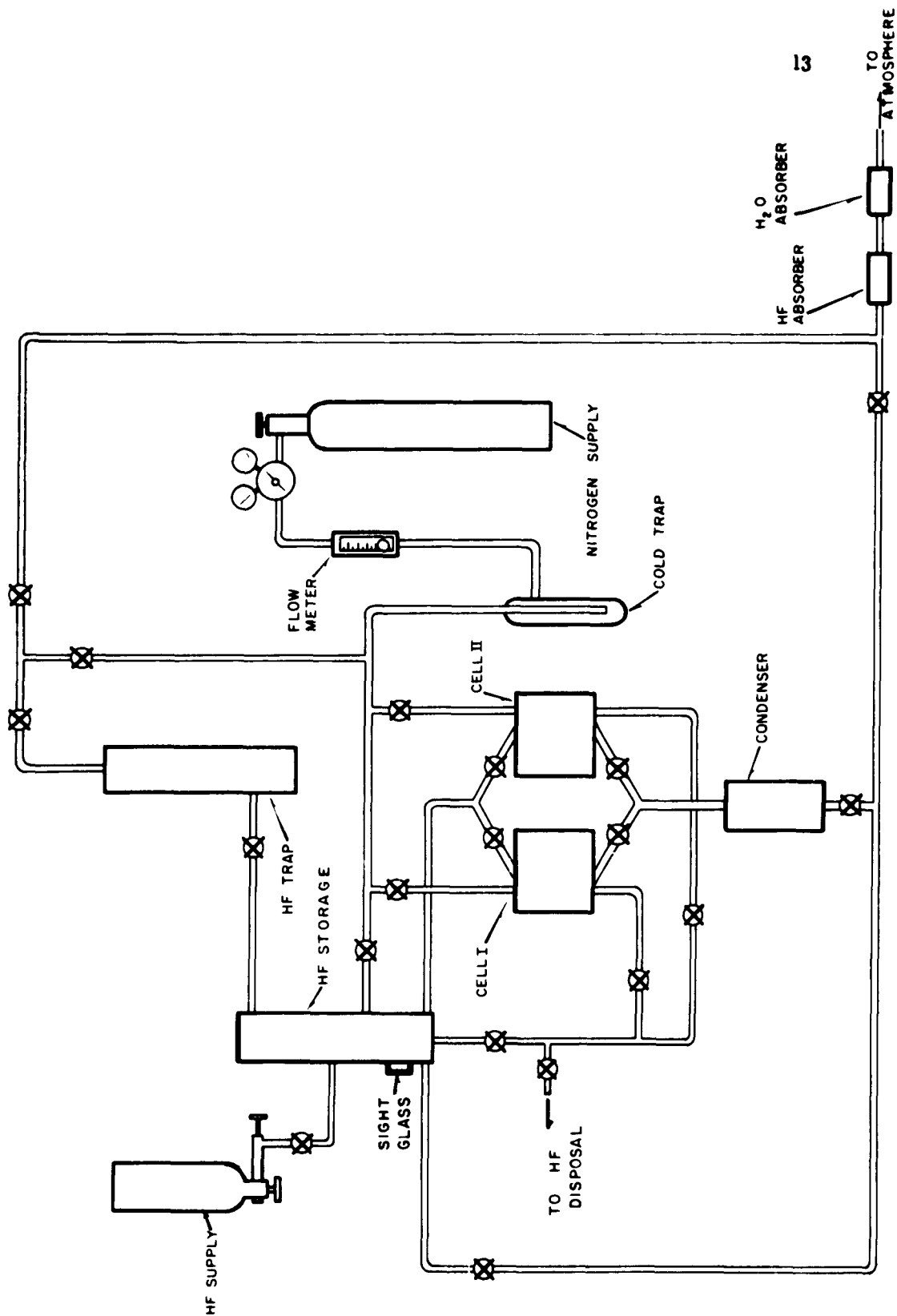
The Hg_2F_2 used in the reference electrodes was made by the following procedure:

1. Dilute solutions of $HgNO_3$ and Na_2CO_3 were prepared using analytical grade crystals and distilled water.

2. The Na_2CO_3 solution was added dropwise to an aliquot of $HgNO_3$ solution until the precipitation of yellow Hg_2CO_3 ceased.

3. The solution was then filtered and the precipitate washed with distilled water.

4. The Hg_2CO_3 was then converted to Hg_2F_2 by adding 48% HF dropwise until CO_2 evolution ceased. The Hg_2F_2 was then recovered by decantation and dried in a vacuum desiccator.

Moist air slowly converts Hg_2F_2 to mercurous oxide; therefore, care was taken to store the Hg_2F_2 under vacuum until needed. The reaction with air is sufficiently slow that the electrodes can be prepared without detectable change in color of yellow Hg_2F_2 to black Hg_2O. Of course, a trace of Hg_2O is not expected to affect performance of the electrodes, as it is converted back to Hg_2F_2 in the anhydrous HF. Contamination by Hg_2O is undesirable, however, as its dissolution releases water into the HF.

The potential difference between freshly prepared pairs of reference electrodes was always within 0.014 v as shown in Table I. In preliminary experiments, two reference electrodes were always placed in the cell with one working electrode. One of the reference electrodes was always maintained at open-circuit conditions to serve as a basis for checking the performance of the other reference electrode which was used in the potentiostat

TABLE I

POTENTIAL DIFFERENCE OF PAIRS OF Hg/Hg_2F_2 ELECTRODES

| ELECTRODE PAIR | ΔE at Open Circuit, volts[a] | | | WORKING ELECTRODE USED |
| | BEFORE POLARIZATION | AFTER POLARIZATION | | |
		Anodic	Cathodic	
1[e]	-0.014	----	----	Aluminum, platinum
2	-0.008	+0.002	-0.016	Aluminum
3[e]	+0.011	----	----	Magnesium
4	+0.003	+0.001[b]	+0.004[c]	Hg/Hg_2F_2
5	+0.014	+0.014[b]	+0.012[c]	Hg/Hg_2F_2[d]

[a] The sign refers to the potential of the electrode in the potentiostat circuit with respect to a like electrode at open circuit.

[b] Open circuit potential after polarization to +1.0 v vs Hg/Hg_2F_2

[c] Open circuit potential after polarization to -1.0 v vs Hg/Hg_2F_2

[d] Cell contained 0.01M NaF in anhydrous HF.

[e] For Electrode Pairs 1 and 3, no values were recorded after polarization.

reference circuit for polarization of the working electrode
(Al, Pt, Mg). These experiments were performed to determine if
the small current (10^{-9} amp) in the reference circuit of the
potentiostat or ions introduced by dissolution of the working
electrode had any adverse effects on the reference electrode. In
later experiments one of the reference electrodes was polarized
to ±1.0 v with respect to another to determine its reversibility
and stability. The open-circuit potentials of the electrodes
after the various experiments are given in the third and fourth
columns of Table I. It should be noted that in all cases except
two, the reference electrode returned to within ±0.002 v of its
original potential after polarization.

New reference electrodes vary widely in potential difference
but approach to within 0.014 v in a few hours as shown in Figure
9. It is assumed that this behavior is due to establishment of
equilibrium between the Hg_2F_2 and Hg in the anhydrous HF and
possibly to effects of traces of Hg_2O in the electrode.

Several polarization curves were obtained for Hg_2F_2 electrodes
in anhydrous HF containing no added electrolyte; however, resis-
tive effects were very high,and the curves could not be reproduced.
However, in a better conducting medium, such as 0.01M NaF in HF,
polarization curves were quite reproducible as shown in Figure 10.
Reversibility of the electrodes is indicated by the symmetry of
the curves and the instantaneous return to open-circuit potential
from +1.0 v and -1.0 v upon removal of the polarizing current.
Attempts were made to record the potential decay of the electrodes;
however, potential decay was faster than the pen speed of the
recorder (1 second full scale). The curves in Figure 10 also
show that polarization of the electrodes is insignificant for
currents which will be encountered (10^{-9} amp) in the potentiostat
reference circuit.

In summary, both the electrochemical properties of this
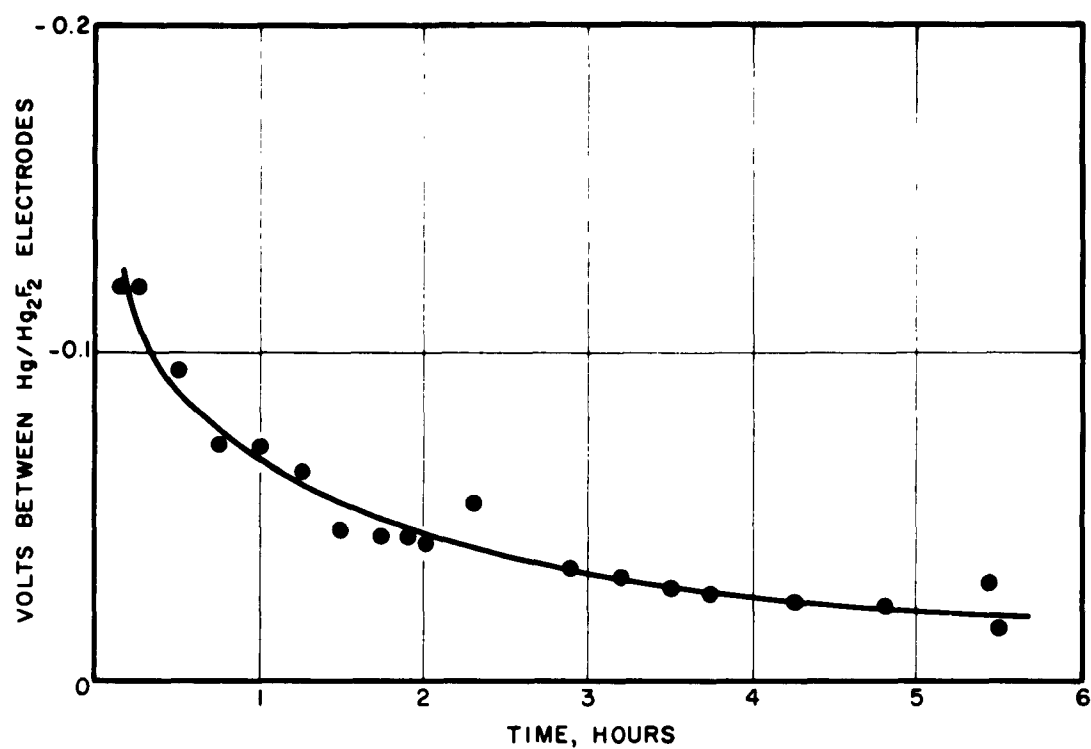electrode system and the physical construction finally developed

Fig. 9 - CHANGE IN OPEN-CIRCUIT POTENTIAL
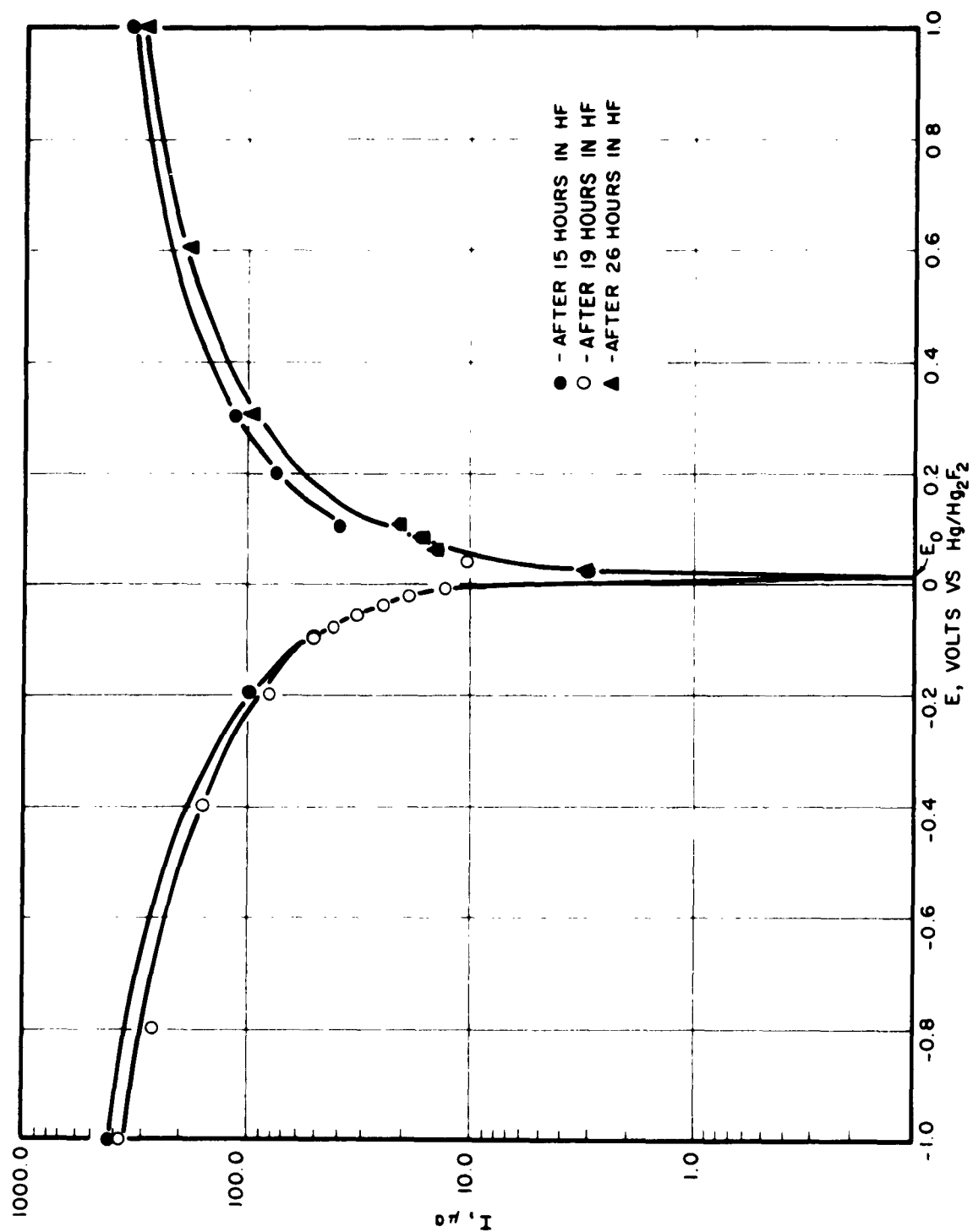OF Hg/Hg_2F_2 REFERENCE ELECTRODE
WITH TIME

Fig.10 - POLARIZATION CURVES OF Hg/Hg$_2$F$_2$ REFERENCE ELECTRODE IN 0.01M NaF

● - AFTER 15 HOURS IN HF
○ - AFTER 19 HOURS IN HF
▲ - AFTER 26 HOURS IN HF

E, VOLTS VS Hg/Hg$_2$F$_2$

I, μα

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IV. WORKING ELECTRODES

During the last quarter several metals were investigated as working electrode materials, includir₃ magnesium, aluminum, thallium, and iron. Of these metals, only magnesium and aluminum resisted extensive attack by the HF. Thallium and iron have been dropped for further consideration.

A. Magnesium

Magnesium was investigated as a possible working electrode because of the low solubility of the fluoride in HF. The solubility of MgF_2 at $-3.3^\circ C$ is 0.025 g/100 g HF (2). Preliminary experiments with magnesium have included weight loss measurements and polarization curves in anhydrous HF. Before each experiment the magnesium (99.95%) wire was cleaned in dilute HCl, thoroughly rinsed, and dried.

Weight loss of a magnesium electrode (after rinsing) at open circuit in anhydrous HF after 15 hours was 0.00055 g for a 10 cm^2 specimen, or 5.5×10^{-5} g/cm^2. Data are insufficient for determination of the corrosion rate after 15 hours. Anodic and cathodic polarization curves of magnesium in anhydrous HF are shown in Figure 11. The low-current level, 1 $\mu a/cm^2$, indicated high polarization caused by an insulating protective coating of MgF_2. The open-circuit potentials of three different magnesium electrodes in anhydrous HF were -0.114, -0.115, and -0.119 v vs Hg/Hg_2F_2. The stability of magnesium electrodes and their reproducible behavior indicate they may be of possible use in electrochemical synthesis of fluorine compounds provided future experiments show that the resistivity of the MgF_2 coating is not too high.

B. Thallium

Thallium forms two stable oxidation states, Tl^+ and Tl^{3+}. Thallous fluoride, TlF, has a much higher solubility in anhydrous HF than does TlF_3. The solubilities of TlF and TlF_3/100 g of HF are 450 g and 0.029 g, respectively, at about $-8.0^\circ C$ (2).
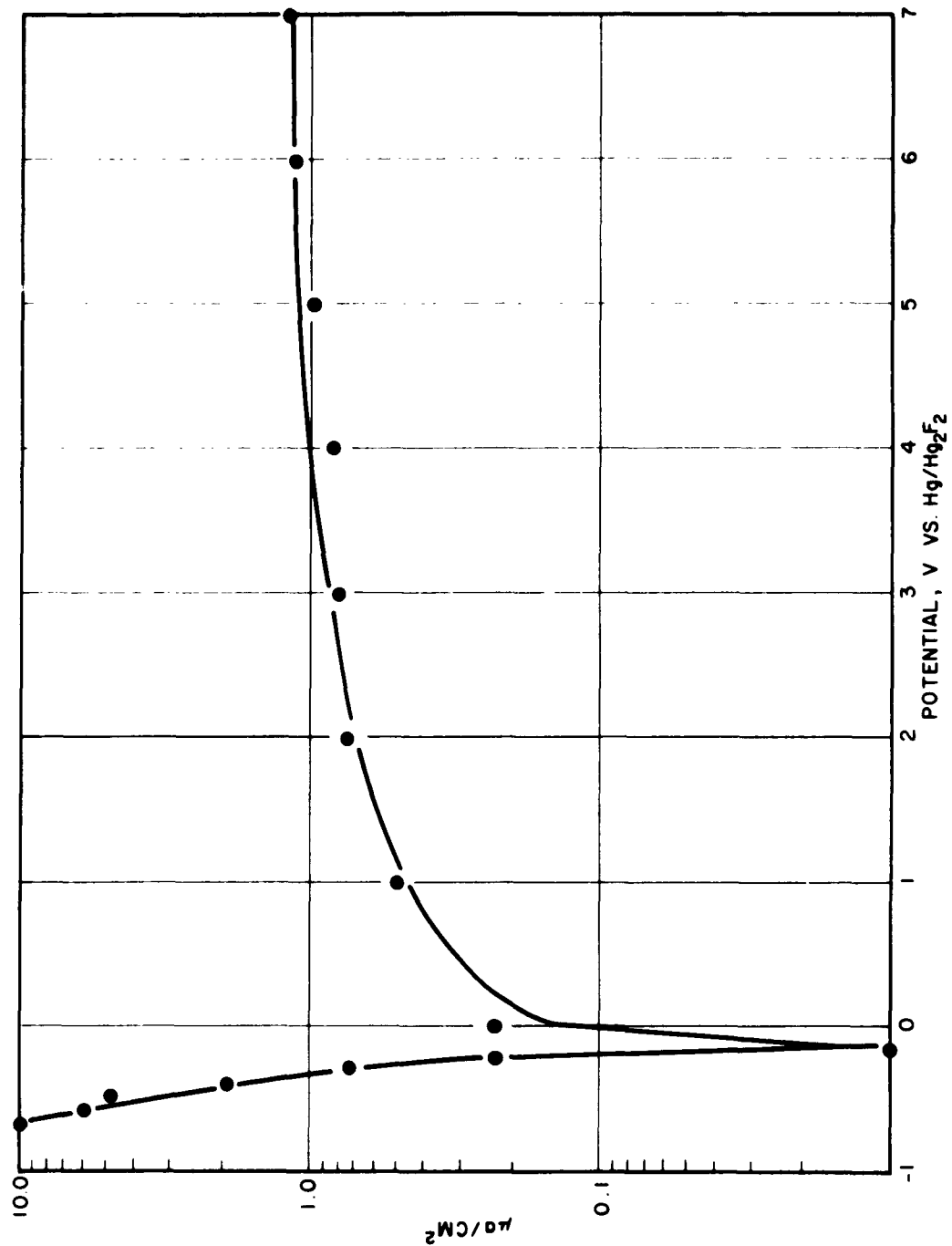
Fig. II - POLARIZATION CURVES OF MAGNESIUM IN ANHYDROUS HF

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At open circuit, thallium dissolved in HF at a tremendous rate, e.g., a 10 cm^2 electrode lost 0.305 g in 30 minutes. Attempts were made to passivate the electrode by immersing it under an applied bias of +10.0 v to oxidize the corrosion product to TlF$_3$; however, corrosion rates were still extremely high. No further work is planned with thallium electrodes.

C. Iron

Corrosion rates of iron electrodes were very high, and no indication of passivity was observed on anodic polarization. On the basis of these results, no further work will be performed with iron.

D. Aluminum

Aluminum electrodes have been investigated extensively and show high resistance to corrosion under conditions of open circuit and anodic polarization. The electrodes used were in the form of 1/8" diameter wires and had the following composition:

Metal	Wt%
Al	99.8+
Fe	0.02
Zn	9.006
Cu	0.002
Ca	Trace
K	Trace

The electrodes were prepared by cleaning in warm dilute HNO$_3$, rinsing with distilled water, then acetone, and finally dried. On exposure to anhydrous HF, the electrodes accumulate a thin coating of AlF$_3$, which results in a weight gain. However, this film is easily washed off by water, and in early experimen_s, the electrodes were weighed with and without the AlF$_3$ coating to determine the loss of aluminum to the HF. However, it was noticed that white crystals continued to grow on the electrodes on exposure to the atmosphere which presumably caused an additional weight

change not directly due to immersion in the HF. After this observation, the AlF_3 film on the electrodes was washed off as quickly as possible after removal from the HF, and weight losses only were recorded.

The weight loss of aluminum in HF as a function of time is shown in Figure 12. It is seen that the major loss occurred the first 5 hours, after which only a very small change takes place up to 40 hours. A few weight losses have been measured for aluminum under anodic bias at +3.0 v and +6.0 v vs aluminum at open circuit. These points have been obtained for periods up to 4 hours as shown in Figure 12 and reflect no change in behavior as compared to electrodes at open circuit.

Polarization curves for aluminum in pure HF have been obtained, but they are not reproducible and show unstable behavior. Several curves will be obtained in solutions of NaF in HF to determine if greater stability can be obtained. Anodic and cathodic polarization curves for aluminum in anhydrous HF are shown in Figure 13. The anodic curve indicates a high degree of polarization which is associated with an equilibrium film growth. The peak in the anodic curve for aluminum repeated in Quarterly Status Report No. 3 is absent on slow polarization or if the aluminum is allowed to stand at open circuit in HF for several hours. On cathodic polarization the protective film is apparently reduced as indicated by the high currents shown in Figure 13. It was noted that after cathodic polarization, the aluminum electrode was severely etched.
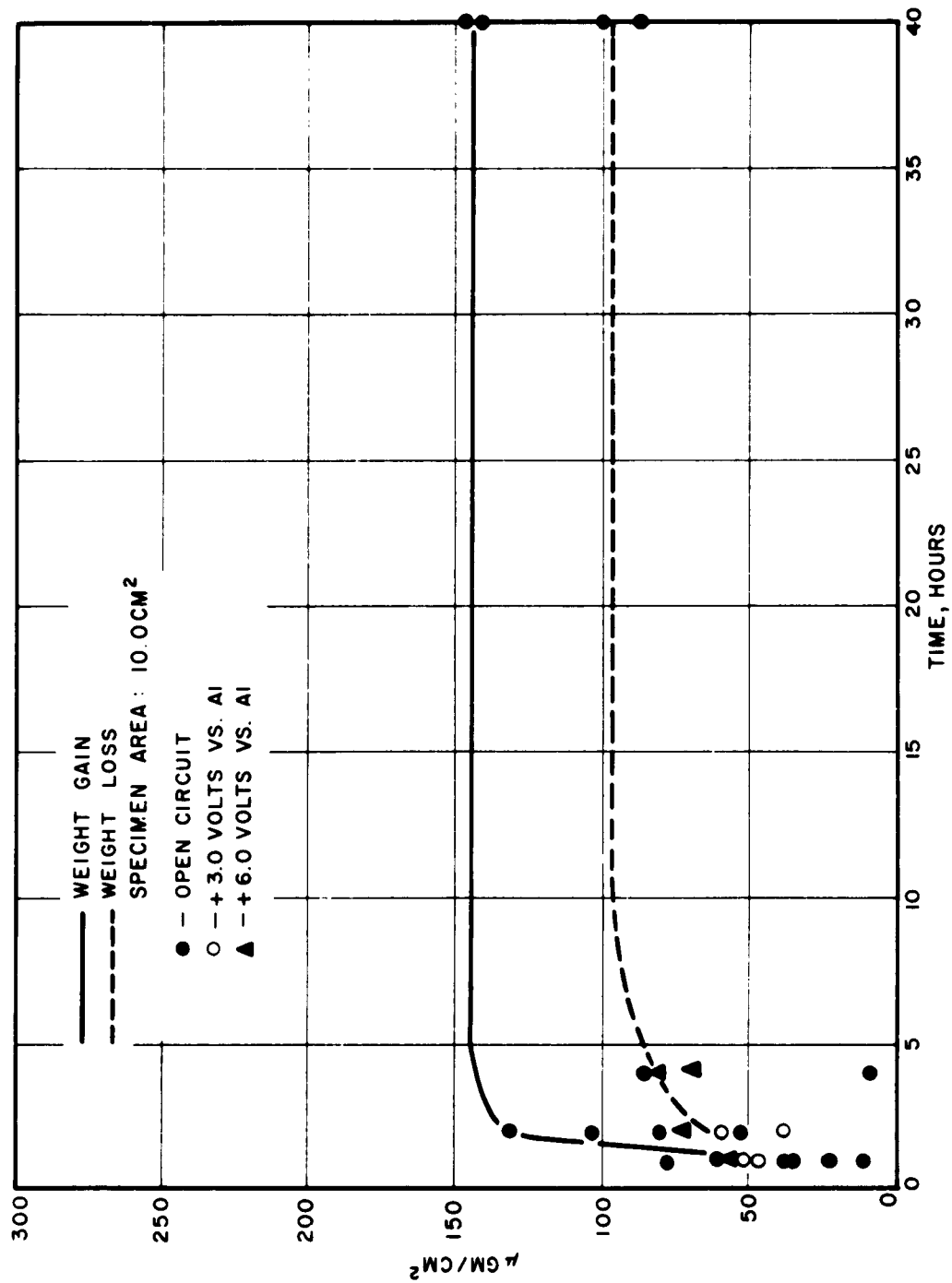
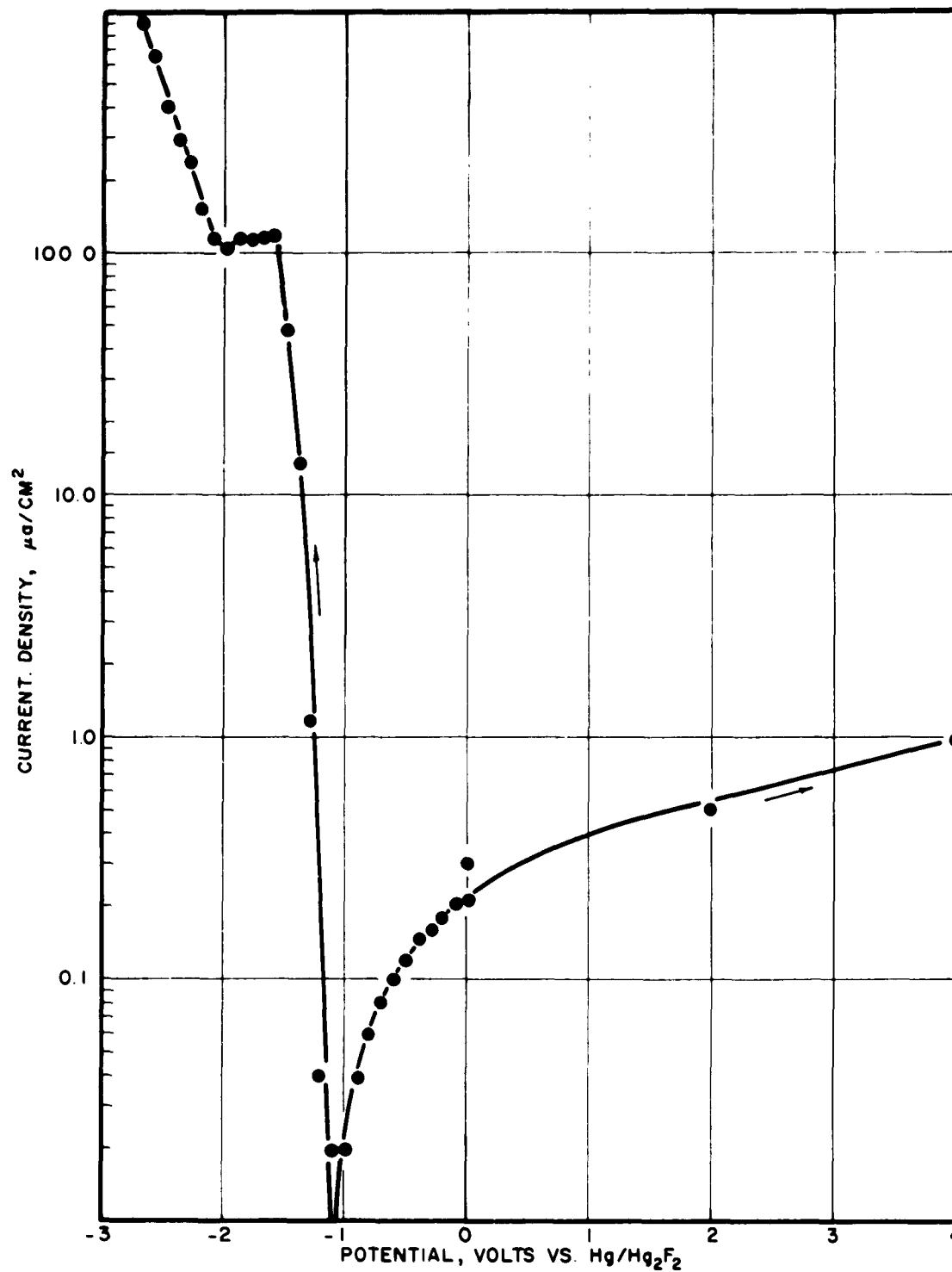Fig.12 - WEIGHT OF FILMED AND DEFILMED ALUMINUM ELECTRODES IN ANHYDROUS HF

Fig. 13 - POLARIZATION CURVES FOR ALUMINUM
IN ANHYDROUS HF

V.   DISCUSSION

The excellent behavior of the Hg/Hg_2F_2 reference electrode will be of immense benefit in future experiments. The difficulty of displacement of the Hg_2F_2 by boiling HF on emptying the cell is not expected to be a handicap, since experiments can be carried out over extended periods of time so long as the HF is maintained below its ambient boiling point.

Work is continuing on the selection of a material for a stable working electrode, although aluminum and magnesium show considerable promise thus far. The polarization curves of aluminum show some conductivity through the protective coating; however, it is not yet known whether this is due to ionic conduction through the film itself or through pores in the film. The high resistivity of the aluminum film will limit fluorination experiments to very dilute solutions. These conditions limit the accuracy of the experiments and will require a greater number of experiments for confident interpretation of the results. It is hoped that better electrode materials are found as the work progresses. One promising material which is to be studied is pyrolytic graphite in the form of rods with the crystal planes concentric to the axis. This configuration should be more resistant to exfoliation than pyrolytic electrodes having the crystal planes exposed to the HF.

VI.   FUTURE COURSE OF THE WORK

The Hg/Hg_2F_2 electrode will continue to serve as the reference electrode in this work, although some slight modifications may be made in the geometry of the electrode holder. Sufficient confidence and skill in preparing the electrodes have been achieved that all experiments can be devoted to studies of working electrodes and fluorination.

Work now in progress consists of studying aluminum and magnesium electrodes in 0.01M solutions of NaF in HF to determine the corrosion current and mode of conductance through the surface films. Other electrode materials, such as chromium and pyrolytic carbon will be investigated.

Some work now in progress is devoted to improving the impurities of HF used in the electrolysis experiments. Anhydrous HF now being used has a resistivity of 10^4 ohms; however, a decrease in resistivity with time is noted. A separate conductivity cell is now being used to determine the optimum fraction to collect in the electrolysis cell from the NaF trap.

TRACOR, INC   1701 Guadalupe St   Austin 1, Texas

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2. Jache, A. W. and Cady, G. H., J. Phys. Chem. $\underline{56}$, 1106 (1952).

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